TRACE ELEMENT DETERMINATIONS OF NORTHWESTERN OHIO CARBONATES

PRESENTED IN FULFILLMENT
OF THE REQUIREMENT OF
GEOLOGY 570

TO
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ABSTRACT

Trace elements in the environment are of two major sources: those inherent in the bedrock and those contributed by man and his activities. When certain of these trace elements become incorporated into a biologic unit in sufficient concentrations, serious threats to the health of the organism may arise. By a study of trace element concentrations in the bedrock of a certain area, one may then begin to gain an insight into what are the relative proportions of the contributions of trace elements into the environment by man or by the environment itself. Also by a study of this sort one may determine certain facts about the environment of formation of the bedrock being examined and a comparison between present environments and ancient ones may be made. Finally by a study of this sort new methods of stratigraphic correlation may be found.

INTRODUCTION

SCOPE OF INVESTIGATION

The general purpose of this investigation was to determine trace element concentrations in the bedrock of northwestern Ohio, in order that one could get some idea of the proportions of trace elements found in the environment today that can be attributed to either the environment itself or to man. This investigation restricted itself to only the bedrock; this was due mostly to lack of time, and it is left to other investigations to study man's contribution of trace elements to the environment. One such investigation is now being undertaken by Tom Schultz, graduate student at Ohio State University. A secondary purpose of this investigation of trace element compositions is that some insight may be gained into what type of conditions were present in the ancient seas in which the bedrock was formed. A final, minor purpose of this investigation was that a new tool in stratigraphic correlation may be gained by analysis of trace elements in bedrock.

Samples were taken over an approximately 4000 square mile area within the Maumee River drainage basin in northwestern Ohio. As the bedrock geology of this area consists of mostly Silurian and Devonian carbonates, only samples of that rock type were collected. Following collection of the samples, atomic absorption techniques were employed to look for five elements (copper, chromium, nickel, lead, cadmium) in each of the samples. After

processing of data, conclusions were reached, and are presented in a further section of this paper.

BACKGROUND AND PREVICUS WORK

A search was undertaken in the literature to determine previous work in the field. Although atomic absorption techniques are recent in the fields of scientific investigation, being introduced in 1955 by Walsh, substantial work has been done in the field and many publications have resulted. A small percentage of these publications were examined and are cited in the bibliography. Work with trace elements, and especially work with trace elements of bedrock, was found to be rare in the literature. It must be realized though, that this search in the literature was far from exhaustive, as this was not the primary purpose of this report. It is my belief, therefore, that aside from a short project undertaken by Sharon Grooms undergraduate student at Ohio State, this is one of the first projects undertaken to determine trace element concentrations of bedrock of northwestern Ohio by atomic absorption techniques.

ACKNOWLEDGEMENTS

My sincere thanks go to Dr. Wayne Pettyjohn, under whom this investigation was undertaken, and to Tom Schultz, a graduate student at Ohio State, whose guidance and help proved invaluable. A special note of thanks goes also to

Carol McKirgan, who typed this paper, and to the Department of Geology at Ohio State, whose facilities and equipment were used throughout the duration of the project.

THEORY AND METHOD OF INVESTIGATION

NATURE OF CARBONATES

Approximately 75% of the total land area of the earth is underlain by sedimentary rocks, and of these, approximately one fifth is made up of carbonate rocks (Ham and Pray, 1961, p.2.). Carbonate rocks are of two major types, limestones and dolomites. Limestone is composed predominately of the mineral calcite, $CaCO_3$, while dolomites are composed mostly of the mineral dolomite, $CaMg(CO_3)_2$. Carbonates are polygenetic, being either marine or fresh water. The carbonates examined in this project all are most likely of marine origin, some being highly fossiliferous and others purely crystalline, and of Silurian and Devonian age. Regardless of specific origin, i.e. either biologic or chemical, the nature of the carbonate rock is determined, or strongly influenced, by the ocean in which it is formed. Thus encased in the rocks found today are vital clues of their origin and of conditions existing in their environments of deposition.

WEATHERING PHENOMENA

Carbon dioxide combines with water to form carbonic acid, which in turn can attack limestones and dolomites according to the following equations (after Longwell, Flint, and Sanders, 1969, p.246.).

$$CO_2 + H_2O \rightarrow H_2CO_3 \rightarrow H^+ + HCO_3^-$$

$$CaCO_3 + 2H^+ \rightarrow H_2O + CO_2 + Ca^{+2}$$

Carbonates can thus easily be dissolved by natural groundwaters, and whatever constituents are in the rock can be released into the environment by groundwater and its surface streams. In the area of the investigation of this report approximately 1000 ft. of bedrock of Silurian and Devonian age have been removed by erosion. (Estimated from Geologic Map of Ohio of J. A. Bownocker) Also, as the areal extent of this investigation covered 4000 square miles, a total volume of over 800 cubic miles of rock have contributed their soluble products to the environment.

ATOMIC ABSORPTION SPECTROPHOTOMETRY

Atomic absorption spectrophotometry as an analytical technique was first introduced by Walsh in 1955. Despite this late start, the technique has found wide acceptance. Atomic absorption is based on the fact that atoms in an unexcited state will become excited when put in a beam of light characteristic of that atom, thus absorbing some of the light. The amount of the light absorbed is proportional to the number of atoms of the particular element present. When standards are introduced the method becomes quantitative.

The basic equipment for atomic absorption spectroscopy consists of a hollow cathode lamp, an atomizing system,

a burner, a monochromator, and a photodetector (Fig. 1.). In the system, the hollow cathode lamp emits light at the particular wavelength of the element being analyzed. This radiation is absorbed in the flame by the atoms of the element. The slightly less intense light is now passed to the photodector by way of the monochromator, which filters out any light other than that characteristic of the element which may have been emitted in the flame.

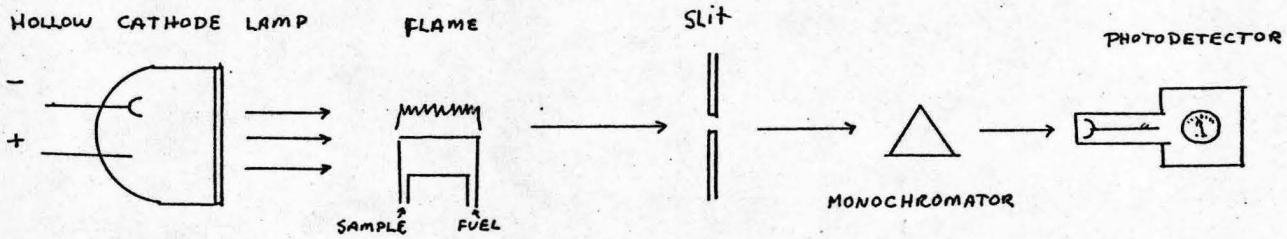


Fig.1. Essential Parts of an Atomic Absorption Spectrophotometer. (After Volborth, 1969, p.196.)

The instrument used in this investigation was the Perkin-Elmer Model 303 with a readout recorder. Specific operation of this instrument is discussed elsewhere in "Instructions, Model 303 Atomic Absorption Spectrophotometer," bulletin 990-9415 of the Perkin-Elmer Company.

COLLECTION OF SAMPLES

A total of 17 samples were collected during the week of December 27, 1971. Collection was over an approximately 4000 square area in northwestern Ohio. The entire area of collection is located in the Maumee River drainage basin. Samples were taken from the following counties: Hardin, Allen, VanWert, Putnam, Paulding, Hancock, Wood, Lucas, Fulton, and Williams.

Geology of the Area

The area of the investigation consists of low lying glaciated land underlain predominantly by carbonate rocks of Silurian and Devonian age (Fig.2.). Carbonates were generally dolomitic, and a large variation from purely crystalline to highly fossiliferous types were found. Structure in the area is relatively simple, being dominated by the Cincinnati Arch. All rocks examined appeared marine in origin. A further, excellent discussion of the geology and structure of the area can be found in the Geologic Survey of Ohio Bulletin 42.

Method of Sample Collection

Samples were taken both from stone quarries and from natural outcrops, although due to the heavy till cover of the Wisconsin glaciations, in very few places do natural exposed sections of the bedrock occur. In each instance the sample was taken as high as possible in the section, as these rocks are the next rocks to be subject to weathering. Efforts were made, however, to collect only fresh, unweathered samples. Samples were put immediately into labeled bags, and location of collection was noted.

Location of Collections (Fig. 3.)

Below is listed, for easy reference, the location of each of the 17 samples collected.

Sample 1: Sample 1 was collected at the former Dunkirk Quarry of the France Stone Company in Dunkirk, in the western part of Blanchard Township, Hardin County.

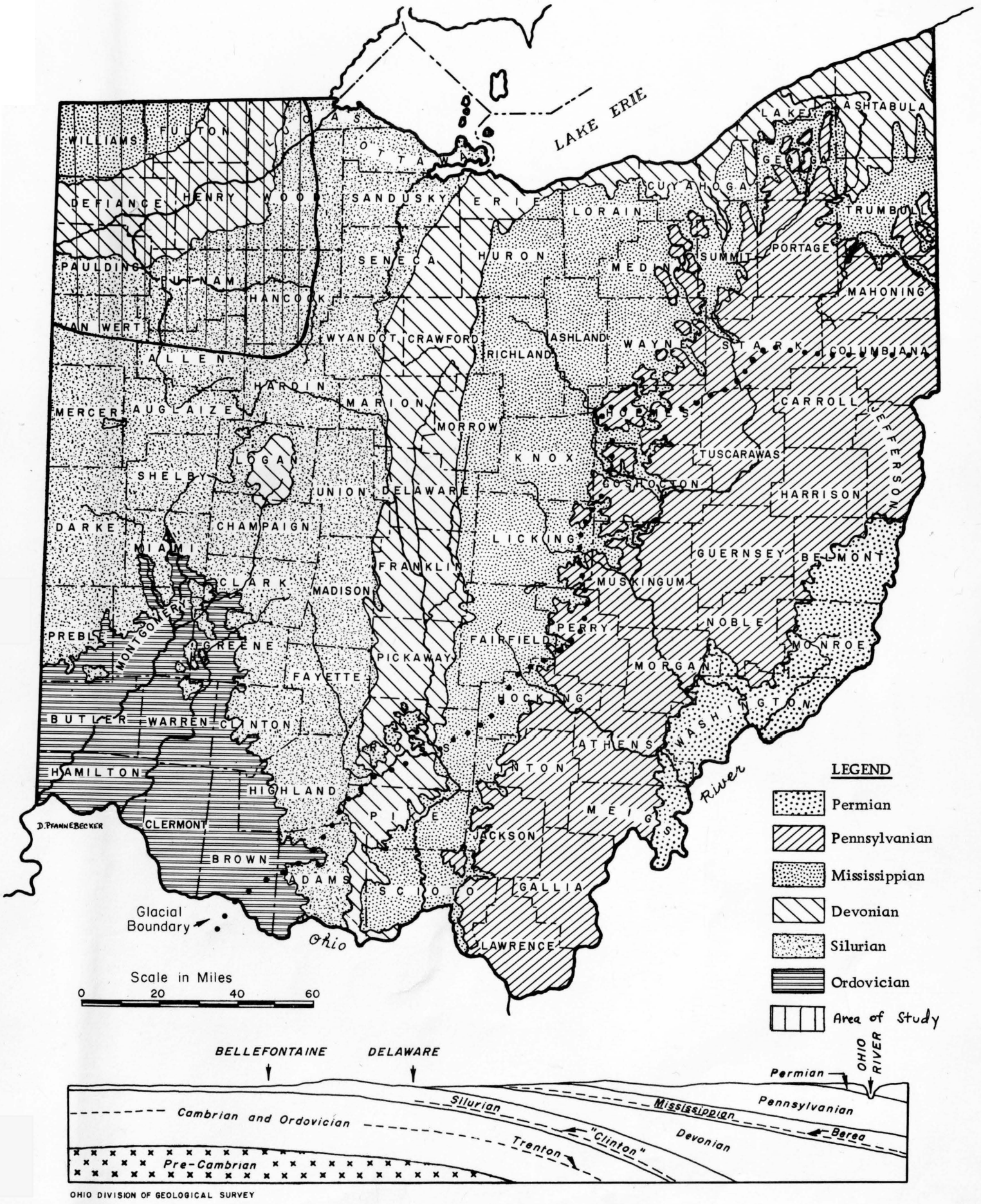


Fig. 2. GEOLOGIC MAP OF OHIO

Fig.3. Location of Collections.

Sample 2: Sample 2 was collected at the Quarry of the Pifer Brothers, 3 miles south of Arlington, in the center of Madison Township, Hancock County.

Sample 3: Sample 3 was collected from an outcrop at the Ottawa River, 2 miles north of Ada, in the north central part of Liberty Township, Hardin County.

Sample 4: Sample 4 was collected at an outcrop near the Bluffton Stone Company in Bluffton, in the northeastern part of Richland Township, Allen County.

Sample 5: Sample 5 was collected along a stream on Highway 12, 3 miles west of Pandora, in the eastern part of Pleasant Township, putnam County.

Sample 8: Sample 8 was collected at the Rimer Plant of the National Lime and Stone Company at Rimer, in the western part of Sugar Creek Township, Putnam County.

Sample 9: Sample 9 was collected at the Delphos Quarries Company in Delphos, in the southeastern part of Washington Township, Van Wert County.

Sample 10: Sample 10 was collected at the former Middlepoint Plant of the France Stone Company in the eastern part of Ridge Township, Van Wert County.

Sample 12: Sample 12 was collected at the former Sylvania Quarry of the France Stone Company, 2 miles southwest of Sylvania in the western part of Sylvania Township, Lucas County,

Sample 13: Sample 13 was collected at the former Monclova Quarry of the France Stone Company, 2 miles north of Monclova, in the northern part of Monclova Township, Lucas County.

Sample 14: Sample 14 was collected on the bank of the Maumee River in Waterville, in the eastern part of Waterville Township, Lucas County.

Sample 15: Sample 15 was collected from the Pugh Stone Quarry in Custar, in the southwest part of Milton Township, Wood County.

Sample 16: Sample 16 was collected at the former Wood County Stone and Construction Company, 3 miles south of Bowling Green, in the northeast corner of Liberty Township, Wood County.

Sample 19: Sample 19 was collected in the bed of a small stream outside the former National Lime and Stone Company, 3 miles west of Mt. Blanchard, in the northeastern part of Madison Township, Hancock County.

Sample 20: Sample 20 was collected at the Paulding Plant of the General Portland Cement Company in Paulding, in the north-eastern part of Paulding, Township, Paulding County.

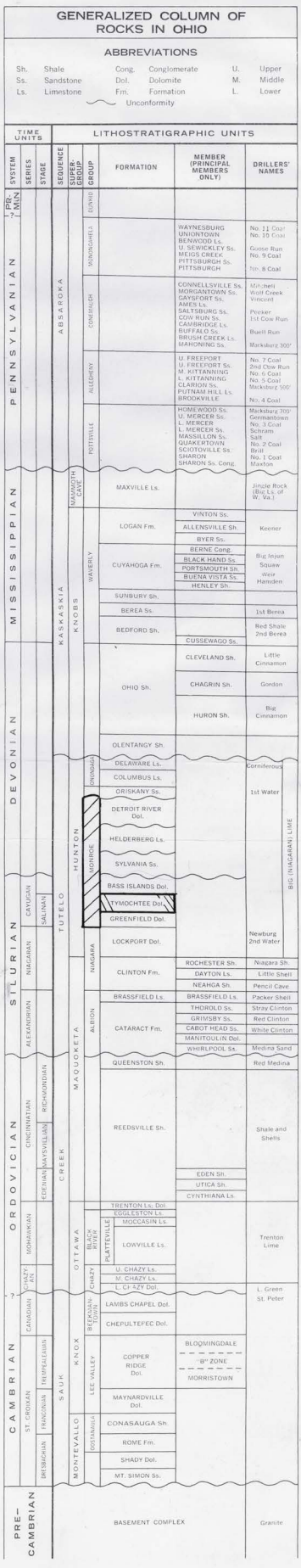
Sample 21: Sample 21 was collected along the Tiffin River on Route 6, in the southern part of Springfield Township, Williams County.

Sample 22: Sample 22 was collected along Ten Mile Creek, in the town of Berkey, in the northern part of Richfield Township, Lucas County.

Stratigraphic Placement of Samples

Although stratigraphic placement of samples was not a primary purpose of this investigation, some effort was

Fig.4. Placement of the Monroe Group and the Tymochtee Dolomite in the geologic section of Ohio.



made to place the samples in the section (Fig.4.). By reference to the Geologic Map of Ohio (Fig.2.) it can be seen that all bedrock in the area of the investigation is of Silurian and Devonian age. By analysis of data in the 1968 Ohio Division Of Mines Report and the Ohio Geological Survey Bulletin 42 some samples can be placed into groups or formations, and are listed below.

Samples 1,3,5,10,13, and 19 are from the Monroe Group.

Samples 2,4,8,9, and 14 are from the Tymochtee Dolomite.

TREATMENT OF SAMPLES

Following collection of samples, a means of getting the rock into solution was needed, as atomic absorption techniques require a liquid sample for determinations to be made. Each sample was first crushed down to about half inch particles and then pulverized to powder form, using the crusher and pulverizer in the rock preparatory laboratory in Mendenhall Laboratory. Hydrochloric acid was used as the solvent following preliminary powdering of the specimens. Various concentrations of acid were tried, and it was found that a 2-Normal acid gave the best rates of reactions. Specific treatment of each sample is as follows:

1) A 400 milliliter beaker was labeled and weighed.

2) Approximately 30 grams of the powdered sample were added and then the beaker and sample were weighed to give the exact weight of the sample.

3) Approximately 400 milliliters of 2-Normal hydrochloric acid was added to the beaker.

4) The beaker with the sample and acid was stirred to facilitate solution

5) The beaker and contents were allowed to stand for two days so that insoluble residues would settle out.

6) The solution was then poured off into volumetric flasks and brought to known volume of 400 milliliters.

7) The remaining insoluble residue was allowed to dry in an oven for 4 or 5 hours to evaporate any remaining moisture.

8) The dry residue and beaker were then weighed. Subtraction of beaker weight gave the insoluble residue weight.

9) The exact weight of sample in solution was then calculated by adding together the solution brought to volume in flasks and the solution evaporated in the oven.

10) Solutions were now ready for analysis on the atomic absorption spectrophotometer.

TRACE ELEMENT DETERMINATIONS

Trace element determinations were made for five elements: Cu, Cr, Ni, Cd, Pb. The Perkin-Elmer Model 303 was used in the determinations. For each sample run an air-acetylene flame was used and the machine was

allowed to warm up for a certain period of time. Minimum warm up times are as follows: 30 minutes for the burner head, 1 hour for the electronics of the machine, and 3 hours for the hollow cathode lamp. Specific operating parameters for each element are listed below.

Cu Determinations

Each of the 17 samples was analyzed for copper on February 3, 1972. Standards of .05 ppm(parts per million), .1 ppm, and.5 ppm were made by simple dilution techniques using 1000 ppm stock solutions. The 3 standards were run before and after the samples to give quantitative meaning to the results. Machine settings were as follows: noise suppression = 30, speed = 10, slit = 3. The multielement hollow cathode lamp was used at a wavelength of 3274.0. A pale blue flame was used. A 2-Normal hydrochloric acid was run as a blank between samples.

Cr Determinations

Chromium was analyzed for on February 4, 1972. Standards of .05 ppm, .1 ppm, and .5 ppm were run with noise suppression = 4, scale expansion = 10, speed = 10, slit = 3. The multielement lamp was used at a , this time the wavelength was set at 2320.0. The flame was adjusted to pale blue. 2-Normal HCL was the blank.

Pb Determinations

Lead was run on February 8, 1972. Standards used were 1.0 ppm and 2.5 ppm. Noise suppression was set at

5, speed = 10, scale expansion = 10, slit = 4. The Pb lamp was used at a wavelength of 2833.1. The flame was pale blue. 2-Normal HCL was the blank.

Ni Determinations

Nickel was run on February 7, 1972. Standards for the run were 1.0 ppm, 2.5ppm 5.0 ppm, and 10.0 ppm. noise suppression = 5, scale expansion = 10, speed = 10, slit = 3. Again the multielement lamp was used; this time the wavelength was set at 2320.0. The flame was adjusted to pale blue. 2-Normal HCL was the blank.

Cd Determinations

Cadmium was run on February 14, 1972. Standards used were .1 ppm and .5 ppm. Noise suppression = 5, scale expansion = 10, speed = 10, slit = 3. The Cd lamp was used at a wavelength of 2288.0. Again a 2-Normal HCL was run as the blank.

Further operating instructions for the Perkin-Elmer 303 may be found in "Instructions, Model 303 Atomic Absorption Spectrophotometer," cited in the bibliography.

RESULTS

Following are listed, for easy reference, the data for each of the 17 samples. Calculations were made as follows::

TOTAL SAMPLE WEIGHT, INSOLUBLE RESIDUE WEIGHT, SAMPLE WEIGHT IN SOLUTION, and VOLUME OF SOLUTION: These calculations are treated under the section of TREATMENT OF SAMPLES.

PPM OF SOLUTION: The parts per million of solution were calculated using the strip chart output of the Perkin-Elmer Model 303 Atomic Absorption Spectrophotometer. A discussion of this method can be found in "Analytical Methods For Atomic Absorption Spectrophotometery", a bulletin put out by the Perkin-Elmer Corporation (No. 303-0152).

PPM OF SAMPLE: The parts per million of the rock sample were calculated by multiplying the volume of solution times the concentration, giving the weight of the particular element in the solution. This value was then divided by the ~~total weight~~ SAMPLE WEIGHT IN SOLUTION of the sample, giving the concentration of the particular element. Results were expressed in milligrams per liter for the solution(ppm), and in milligrams per 1000 grams for the sample rock.

The original strip charts from the sample runs are included in the envelope on the back cover of this report for reference.

SAMPLE 1

TOTAL SAMPLE WEIGHT 30.1 g.

INSOLUBLE RESIDUE WEIGHT 5.0 g

SAMPLE WEIGHT IN SOLUTION 25.1 g

VOLUME OF SOLUTION 418.6 ml.

PPM OF SOLUTION:

Cu	.505
Cr	.165
Ni	11.30
Pb	2.05
Cd	.075

PPM OF SAMPLE:

Cu	8.40
Cr	2.75
Ni	188.4
Pb	34.2
Cd	1.23

SAMPLE 2

TOTAL SAMPLE WEIGHT 30.1 g.

INSOLUBLE RESIDUE WEIGHT 4.4 g.

SAMPLE WEIGHT IN SOLUTION 25.7 g.

VOLUME OF SOLUTION 419.2 ml.

PPM OF SOLUTION:

Cu	.505
Cr	.103
Ni	11.60
Pb	1.82
Cd	.090

PPM OF SAMPLE:

Cu	8.25
Cr	1.67
Ni	189.1
Pb	29.7
Cd	1.48

SAMPLE 3

TOTAL SAMPLE WEIGHT 30.4 g.

INSOLUBLE RESIDUE WEIGHT 3.4 g.

SAMPLE WEIGHT IN SOLUTION 27.0 g.

VOLUME OF SOLUTION 409.8 ml.

PPM OF SOLUTION:

Cu	.502
Cr	.085
Ni	11.40
Pb	1.97
Cd	.106

PPM OF SAMPLE:

Cu	7.63
Cr	1.30
Ni	172.9
Pb	29.9
Cd	1.52

SAMPLE 4

TOTAL SAMPLE WEIGHT 30.0 g.

INSOLUBLE RESIDUE WEIGHT 6.1 g.

SAMPLE WEIGHT IN SOLUTION 23.9 g.

VOLUME OF SOLUTION 422.3 ml.

PPM OF SOLUTION:

Cu	.467
Cr	.183
Ni	10.90
Pb	2.28
Cd	.093

PPM OF SAMPLE:

Cu	8.24
Cr	3.22
Ni	192.5
Pb	40.3
Cd	1.63

SAMPLE 5

TOTAL SAMPLE WEIGHT 31.2 g.

INSOLUBLE RESIDUE WEIGHT 2.1 g.

SAMPLE WEIGHT IN SOLUTION 29.1 g.

VOLUME OF SOLUTION 407.5 ml.

PPM OF SOLUTION:

Cu	.505
Cr	.052
Ni	11.85
Pb	2.15
Cd	.106

PPM OF SAMPLE:

Cu	7.08
Cr	.721
Ni	165.9
Pb	30.1
Cd	1.48

SAMPLE 8

TOTAL SAMPLE WEIGHT 30.3 g.

INSOLUBLE RESIDUE WEIGHT 2.8 g.

SAMPLE WEIGHT IN SOLUTION 27.5 g.

VOLUME OF SOLUTION 407.8 ml.

PPM OF SOLUTION:

Cu	.485
Cr	.100
Ni	11.02
Pb	2.07
Cd	.100

PPM OF SAMPLE:

Cu	7.20
Cr	1.49
Ni	163.3
Pb	30.7
Cd	1.49

SAMPLE 9

TOTAL SAMPLE WEIGHT 30.0 g.

INSOLUBLE RESIDUE WEIGHT 1.1 g.

SAMPLE WEIGHT IN SOLUTION 28.9 g.

VOLUME OF SOLUTION 404.3 ml.

PPM OF SOLUTION:

Cu	.550
Cr	.070
Ni	11.20
Pb	2.03
Cd	.077

PPM OF SAMPLE:

Cu	7.68
Cr	.969
Ni	156.7
Pb	28.4
Cd	1.07

SAMPLE 10

TOTAL SAMPLE WEIGHT	30.6 g.
INSOLUBLE RESIDUE WEIGHT	.6 g.
SAMPLE WEIGHT IN SOLUTION	30.0 g.
VOLUME OF SOLUTION	402.3 ml.

PPM OF SOLUTION:

Cu	.530
Cr	.068
Ni	12.00
Pb	2.51
Cd	.131

PPM OF SAMPLE:

Cu	7.10
Cr	.900
Ni	161.0
Pb	33.7
Cd	1.77

SAMPLE 12

TOTAL SAMPLE WEIGHT 30.5 g.

INSOLUBLE RESIDUE WEIGHT 3.6 g.

SAMPLE WEIGHT IN SOLUTION 26.9 g.

VOLUME OF SOLUTION 405.9 ml.

PPM OF SOLUTION:

Cu	.660
Cr	.170
Ni	12.10
Pb	1.90
Cd	.124

PPM OF SAMPLE:

Cu	9.96
Cr	2.56
Ni	182.5
Pb	28.7
Cd	1.86

SAMPLE 13

TOTAL SAMPLE WEIGHT 30.2 g.

INSOLUBLE RESIDUE WEIGHT 2.6 g.

SAMPLE WEIGHT IN SOLUTION 27.6 g.

VOLUME OF SOLUTION 409.1 ml.

PPM OF SOLUTION:

Cu	.485
Cr	.043
Ni	11.40
Pb	2.87
Cd	.177

PPM OF SAMPLE:

Cu	7.17
Cr	.652
Ni	168.8
Pb	42.4
Cd	2.61

SAMPLE 14

TOTAL SAMPLE WEIGHT 30.8 g.

INSOLUBLE RESIDUE WEIGHT 3.0 g.

SAMPLE WEIGHT IN SOLUTION 27.8 g.

VOLUME OF SOLUTION 4134 ml.

PPM OF SOLUTION:

Cu	.485
Cr	.063
Ni	11.20
Pb	1.82
Cd	.150

PPM OF SAMPLE:

Cu	7.19
Cr	1.00
Ni	166.5
Pb	27.1
Cd	2.23

SAMPLE 15

TOTAL SAMPLE WEIGHT 30.5 g.

INSOLUBLE RESIDUE WEIGHT 2.9 g.

SAMPLE WEIGHT IN SOLUTION 27.6 g.

VOLUME OF SOLUTION 411.0 ml.

PPM OF SOLUTION:

Cu	.570
Cr	.247
Ni	11.75
Pb	2.18
Cd	.165

PPM OF SAMPLE:

Cu	8.48
Cr	3.69
Ni	175.0
Pb	32.5
Cd	2.46

SAMPLE 16

TOTAL SAMPLE WEIGHT 30.5 g.

INSOLUBLE RESIDUE WEIGHT .5g.

SAMPLE WEIGHT IN SOLUTION 30.0 g.

VOLUME OF SOLUTION 403.1 ml.

PPM OF SOLUTION:

Cu	.540
Cr	.223
Ni	11.70
Pb	2.50
Cd	.119

PPM OF SAMPLE:

Cu	7.27
Cr	3.00
Ni	157.3
Pb	33.7
Cd	1.6

SAMPLE 19

TOTAL SAMPLE WEIGHT 30.2 g.

INSOLUBLE RESIDUE WEIGHT 6.5 g.

SAMPLE WEIGHT IN SOLUTION 23.7 g.

VOLUME OF SOLUTION 423.8 ml.

PPM OF SOLUTION:

Cu	.502
Cr	.170
Ni	10.10
Pb	2.33
Cd	.127

PPM OF SAMPLE:

Cu	8.99
Cr	3.04
Ni	180.6
Pb	41.6
Cd	2.28

SAMPLE 20

TOTAL SAMPLE WEIGHT	30.0 g.
INSOLUBLE RESIDUE WEIGHT	2.0 g.
SAMPLE WEIGHT IN SOLUTION	28.0 g.
VOLUME OF SOLUTION	407.9 ml.

PPM OF SOLUTION:

Cu	.780
Cr	.056
Ni	20.60
Pb	2.72
Cd	.182

PPM OF SAMPLE:

Cu	11.4
Cr	.821
Ni	300.0
Pb	39.6
Cd	2.64

SAMPLE 21

TOTAL SAMPLE WEIGHT 30.0 g.

INSOLUBLE RESIDUE WEIGHT 1.2 g.

SAMPLE WEIGHT IN SOLUTION 28.8 g.

VOLUME OF SOLUTION 403.8 ml.

PPM OF SOLUTION:

Cu	.502
Cr	.082
Ni	10.50
Pb	2.53
Cd	.135

PPM OF SAMPLE:

Cu	7.05
Cr	1.39
Ni	147.2
Pb	35.4
Cd	1.91

SAMPLE 22

TOTAL SAMPLE WEIGHT 30.4 g.

INSOLUBLE RESIDUE WEIGHT 2.1 g.

SAMPLE WEIGHT IN SOLUTION 28.3 g.

VOLUME OF SOLUTION 407.2 ml.

PPM OF SOLUTION:

Cu	.495
Cr	.292
Ni	10.90
Pb	1.97
Cd	.170

PPM OF SAMPLE:

Cu	7.14
Cr	4.20
Ni	156.9
Pb	28.3
Cd	2.44

ANALYSIS OF RESULTS

CONCENTRATIONS

Averages for the trace element concentrations are as follows:

Cu	8.01 ppm
Cr	1.96 ppm
Ni	178.44 ppm
Pb	33.31 ppm
Cd	1.86 ppm

Values given in Rankama (1950) for limestones and dolomites from other areas are as follows (method of analysis was not given, and unless specifically noted locations were not given):

Cu (average for limestones)	20.2 ppm
Cu (average for dolomites)	12.6 ppm
Cr (carbonate sample from Southern Lapland)	2.0 ppm
Ni (limestone from Sweden)	3.0 to 10.0 ppm
Cd (no values given)	
Pb (average of limestones)	5.0 to 32.6 ppm

Thus it can be seen that values found in this investigation agree well with Rankama's for Cr. Cu values found in this investigation are somewhat low, Pb slightly high, and Ni very high. Cd values are offered here as there are no values for Cd given by Rankama. The values for Ni found in this investigation are so much higher than values given by Rankama that more work with Ni in the area of this investigation needs to be done.

High values found in this investigation and corresponding sample numbers are as follows:

Cu	11.40 ppm	(Sample 20)
Cr	4.20 ppm	(Sample 22)
Ni	300.00 ppm	(Sample 20)
Pb	42.40 ppm	(Sample 13)
Cd	2.64 ppm	(Sample 20)

Low values and corresponding sample numbers are as follows:

Cu	7.05 ppm	(Sample 21)
Cr	.652 ppm	(Sample 13)
Ni	147.2 ppm	(Sample 21)
Pb	27.1 ppm	(Sample 14)
Cd	1.07 ppm	(Sample 9)

Thus it can be seen that Sample 20 was highest in 3 categories (Cd, Ni, Cu) and that Sample 21 was lowest in 2 categories (Cu, Ni). Another fact found in the data is that Sample 13 is highest in Pb but lowest in Cr. An analysis of atomic radii of these elements may give some explanation of these occurances (values from Sargent-Welch Periodic Table of the Elements).

ELEMENT	ATOMIC RADIUS IN ANGSTROMS
Cu	.69
Cr	.69
Ni	.72

Pb	1.20
Cd	.97

The close association of Ni and Cu as either high or low values may be due to their closeness of atomic radii, and the association of high Pb and low Cr may be due to their large differences in radii. It would seem that conditions were such in the case of Sample 20 that the chemical environment was favorable for allowing elements with an atomic radius of about .70 into the lattice, and that in the case of Sample 21 conditions were not favorable. In the case of Sample 13 conditions were right for allowing an element with a radius of 1.20 but not one of about .70. Thus conditions seem to be similar in Sample 21 and 13 and different in Sample 20. The geochemistry of carbonate environments is not the primary purpose of this report, but here appears to be a start in determining ancient environments, and certainly work needs to be done in this area.

ISOCONS

An attempt was made to see how concentrations varied within a certain stratum. As stratigraphic placement of samples was difficult; the following maps are only very rough approximations, if they are valid at all. Plotted on the following base maps (Figs. 5-9.) are sample locations with accompanying concentrations. Sample locations used are those from the supposedly known strata of the Monroe Group (points from Tymochtee Dolomite are also plotted as this

formation is included in the Monroe Group). If concentrations of certain sample locations did not fit in, they were not included on the map, the assumption here being(perhaps erroneous) that the stratigraphic placement was in error. As no such attempt of this sort had been found in the short search through the literature, the term "isocon", for lines of equal concentration, is suggested. Thus the following maps are offered as a start in an analysis of this type, and certainly refinement and more work needs to be done to confirm the validity of these maps.

Fig.5. Isocon map for Cu. See explanation in text (p.41.).

Fig.6. Isocon map for Ni. See explanation in text (p.41.).

Fig.7. Isocon map for Cr. See explanation in text (p.41.).

Fig.8. Isocon map for Pb. See explanation in text (p.41.).

Fig.9. Isocon map for Cd. See explanation in text (p.41.).

CONCLUSIONS

HEALTH ASPECTS

As stated previously in this paper, certain concentrations of trace elements can be harmful to living organisms. As these trace elements have two major sources, those from the natural environment itself and those contributed by man, only when quantitative facts are known about one can quantitative statements be made about the other. This paper has been concerned with trace elements which may be released into the environment by bedrock. Certainly an area which has a high concentration of a particular element in the bedrock will reflect this high concentration by the element being found in the ground water and the soil of the area. As stated before in this paper, over 800 cubic miles of bedrock have contributed their soluble products to the environment in the area of this investigation. Although this has happened over a period of millions of years, certainly these soluble products are reflected in past waters and soils and in present waters and soils. It would be interesting to see if any correlation exists between certain diseases being common in an area and a certain trace element concentration, although this is far beyond the scope of this report. Thus the results of this report are presented to be used by other people making similar examinations, and as a start in making trace element concentrations in the environment quantitative. In any case much work needs to be done in the area of this report.

ANCIENT ENVIRONMENTS

As previously stated in this paper a rock will reflect its environment of formation. By analysis of its major components a rock can expose valuable information on conditions of the past. Papers have appeared on this subject and are too numerous to mention. Much less work, however, has been done using trace elements as environmental indicators. One such work by Turekian (1963) uses boron and strontium concentrations as measurements of ancient salinities, and as stated in the section of this paper on ANALYSIS OF RESULTS, certain patterns of element associations seem evident, and may possibly later be used as environmental indicators. But as stated before, much more work in this area needs to be done.

METHOD OF CORRELATION

The possibility exists of using trace elements in stratigraphic correlation. A discussion by Turekian (1963) states that correlation can be attempted, but it usually leads to ambiguous results. An attempt was made in this experiment to verify Turekian's statement. An extra sample (taken from the same location as Sample 2) was analyzed and an attempt was made to see how closely these results agreed with the results of the actual Sample 2. Below is listed the concentrations of elements in Sample 2 and the "unknown."

	Sample 2	"Unknown"
Cu	8.25 ppm	8.20 ppm
Cr	1.67 ppm	1.20 ppm
Ni	189.1 ppm	192.2 ppm
Pb	29.7 ppm	37.6 ppm
Cd	1.48 ppm	2.76 ppm

Thus it can be seen that some agreement is present and also some variance. It is doubtful that results agree enough for direct stratigraphic correlation. Possibly future refinements in trace element determinations may make correlations possible, but in the meantime much work needs to be done.

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Bill fine

1, 3, 5, 10, 13, 19 Monroe Gp.

2, 4, 8, 9, 14 Tymochtee Dolo

Monroe

	1	3	5	10	13	19
Cu	8.40	7.63	7.08	7.10	7.17	8.99
Cr	2.75	1.30	.721	.900	.652	3.04
Ni	188.4	172.9	165.9	161.0	168.8	180.6
Pb	34.2	29.9	30.1	33.7	42.4	41.6
Cd	1.23	1.52	1.48	1.77	2.61	2.28

Tymochtee

	2	4	8	9	14
Cu	8.25	8.24	7.20	7.68	7.19
Cr	1.67	3.22	1.49	.969	1.00
Ni	189.1	192.5	163.3	156.7	166.5
Pb	29.7	40.3	30.7	28.4	27.1
Cd	1.48	1.63	1.49	1.07	2.23

Included in this envelope are the original strip charts from the trace element determinations. Figures in green are sample numbers and standards (underlined). Numbers in black ink are peak heights, and numbers in pencil with parentheses are concentrations of solutions.